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TECHNICAL MEMORANDUMS

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

No. 553

EXPERIMENTAL INVESTIGATIONS CONCERNING THE LIMITS OF DETONATION IN GASEOUS MIXTURES

By Rudolf Wendlandt

PART I

From Zeitschrift für Physikalische Chemie 110, 637, (1924)

Washington
February, 1930

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

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PART I

I. Introduction

Data available

The spread of the ordinary flame through an explosive mixture of gases depends in every respect on the influence of the experimental conditions imposed upon it (References 1, 2, and 3). It is, therefore, little to the point to speak of explosion limits or of flame velocity in terms of per cent composition of the explosive gases. All data of this nature really rest on the kind of ignition, its position, the form and material of the container and on the way the reaction runs its course; in short, upon the conditions imposed upon the reaction by the experimental method employed, as temperature and pressure. Under the same conditions imposed the same set of results may well be obtained. The explosive limits of various gaseous mixtures have frequently been investigated often under the most variable conditions leading to greatly dissimilar results.

But the very first intensive investigation of detonation, that carried out by Berthelot and Vieille (Reference 4 - see also Nernst - Reference 5) showed, on the contrary, a remarkable agree-

*From Zeitschrift für Physikalische Chemie 110, 637, 1924.

ment of results. In this form of reaction characterized by unusually high speed of propagation and high pressure of the quasi-stationary wave, the process as observed in long tubes showed a constant detonation velocity, characteristic for each explosive mixture, that was independent of the course traversed, of the material of the container and, above a certain diameter, independent of the cross section of the tube. In what follows we shall confine ourselves to a consideration of the process having the following characteristics recognized as normal detonation: a plane compressional wave front behind the flame and a constant high velocity of propagation over long stretches of the observation tube. The limits of the possibility of detonation in a gaseous mixture have been as yet only casually considered in any experimental or theoretical study of the detonation process. The determining conditions yet remain unexplained although they would be in themselves of interest and for a further knowledge of this form of reaction, indispensable. Besides, a knowledge of the limits of detonation in gaseous mixtures is also of significant practical interest. It is the purpose of this investigation to determine quantitatively these limits for the conditions imposed and for a number of given gaseous explosive mixtures. By this means it is hoped to arrive at some generalized explanation. The problem therefore is not simply to produce detonation, but rather to determine the conditions under which the quasi-stationary detonation wave is propagated when

the conditions for its generation at some place are given. That there are evidently many explosive gases that do not meet this last condition and fail to support a quasi-stationary wave, is known. This fact is not without its technical significance; yet this phase of the process has received little experimental or theoretical attention.

For the case of explosive mixtures much diluted by inert gases, or possessing in themselves a low potential energy, the data given by Berthelot and Vieille are not utilizable. Their values are too low by as much as 100 meters per second. Careful measurements made by Dixon (Reference 6) have shown that to obtain consistent results in these cases tubes of greater diameter and a higher ignition energy were required; while in the case of pure electrolytic gas, $2\ H_2 + O_2 \rightarrow$, the detonation wave showed no change in velocity in passing from a tube of 5 mm diameter to one of 9 mm. Dixon found that even tubes of 9 mm diameter failed to give constant results in the case of very weak or very dilute explosive mixtures. In his experimental work he used a lead tube of 13 mm diameter and 100 meters long. This tube was wound on a reel 2 ft. in diameter. The data of Dixon does not suffice to establish detonation limits. He mentions only two cases at initial atmospheric pressure where the detonation wave did not develop in the 13 mm tube: $2\ H_2 + O_2 + 7\ N_2 \rightarrow$, and $C_2 N_2 + O_2 + 3\ N_2 \rightarrow$. Besides these two cases he mentions two other mixtures where variable speeds were observed or where

detonation did not take place: $H_2 + N_2O + 2\ N_2$, 1650 m/s, 1416 m/s; $2\ CH_4 + 3\ O_2 + 5\ N_2$, 1888 m/s, 1872 m/s (goes out sometimes). The following mixtures observed by Dixon contained one or two mols less N_2 and exhibited a normal process of detonation: $2\ H_2 + O_2 + 5\ N_2$, 1815 m/s; $C_2N_2 + O_2 + 2\ N_2$, 2166 m/s. These few cases are not sufficient to determine what conditions limit the formation of a normal detonation wave. Indeed it would appear from these results that greatly diluted or weak explosive mixtures show no definite speed of propagation. The data is also so insufficient that it leaves the question open if tube diameter would not have considerable influence on the rate of explosive reaction in weak or highly diluted mixtures. Other than the cases mentioned above, the only data existing on weak or greatly diluted mixtures, is that given by Le Chatelier (Reference 7); (see also Berthelot and Le Chatelier - Reference 8) who, as Dixon, gives only three cases. The explosion tube used in his experiments had a diameter of only 10 mm and at some points in its length was constricted to even less diameter. In passing these constricted points the detonation wave corresponding to his so-called "limiting mixtures" would fail and again automatically restore itself. Besides this, his method of ignition does not seem suitable. His data is not sufficient in quantity nor quality to determine a detonation limit. Le Chatelier connected the statements he made concerning detonation limits with the appearance of the flame trace in his photo-

graphs and concluded that the detonation wave preceded the flame by a number of centimeters! Dixon (Reference 14) in his excellent series of studies of the detonation wave calls this statement in question. The point will be considered again in the theoretical analysis to follow.

II. The Experimental Arrangement

A long, transparent detonation tube is filled with an explosive gaseous mixture. By appropriate initial ignition at one end of the tube, the detonation wave was introduced into the gaseous mixture to be examined. If this mixture proves capable of supporting a detonation wave, such a wave will be propagated along the tube with very great constant velocity. This constant velocity is the criterion of a detonating process within the gases, and its magnitude is to be quantitatively determined. Naturally there are also a number of other features accompanying the process that are to be noted, especially that of flame appearance.

1. Preparation, Storing and Analysis of the Gaseous Mixtures.- The investigation was carried out with hydrogen-air mixtures, with carbon monoxide-air mixtures, and with mixtures of carbon monoxide and oxygen. The hydrogen used was produced from a 30% sodium hydroxide solution by electrolysis, using nickel electrodes. The gas was then led through an electrically heated platinum-asbestos tube, then through concentrated sul-

phuric acid and finally stored over water in a copper gasometer of 20 or 30 liters capacity. This gasometer was provided with a glass gauge and millimeter scale and contained beforehand the requisite amount of air for the preparation of the desired mixture to be used. The carbon monoxide was prepared from 95% formic acid and concentrated sulphuric acid, washed through potassium hydroxide and stored with the requisite amount of air or of oxygen also in a copper gasometer. The mixtures so prepared were left for a number of hours - never longer than a day - in order that complete diffusion might take place. They were then analyzed just before the experiments were carried out. Gas samples taken and analyzed from the gaseous mixture after passing through the explosion tube in the filling operation checked with the analysis of the gases in the gasometer.

The electrolytic gas ($2\ H_2 + O_2$) used in producing the initial detonation wave for ignition was stored in a separate gasometer - a burette arranged according to Hempel served for analysis of the gases. Hydrogen was burned in a palladium-asbestos capillary according to Winkler (Reference 9). If the mixture of carbon monoxide is led through the heated palladium-asbestos capillary two or three times, then immediately to the

attached KOH pipette, exact results in the absence of other combustible gases are obtained quicker than by the usual method of absorption in ammonium-calcium-copper chlorate after previous oxygen absorption. For comparison with the gases from the explosion tube this procedure has its advantages.

For the investigation of dried gases, the mixture was passed over calcium chloride and then through two flasks of concentrated sulphuric acid into the explosion tube that was previously dried by a stream of dried air.

For investigation of explosive mixtures at water-vapor saturation, the gases held over water in the gasometers at room temperature were passed through wash bottles, then through a water mantel held at constant temperature.

2. The Detonation Tube. The Initial Detonation Wave.- As a container of the gaseous explosive mixture to be investigated, a Jena hard glass tube L of 21 mm diameter was used (Fig. 1). This tube was attached to a wooden support H. The ignition of the explosive gases contained in this tube required an ignition device as positively defined and accurate as possible and yet not so violent as to injure the apparatus. To meet these conditions there was attached to one end of the glass tube a tube of steel E of the same diameter 130 cm long. This could be

filled with electrolytic gas, $2 H_2 + O_2$. The steel tube was provided with a gas-tight stopcock at the end adjoining the glass tube. Ten centimeters from the other end it was provided with an insulated spark gap of thick copper wire attached to a powerful induction coil. The glass and steel tubes, together with the separate lengths of the glass tube were bound together by brass flanges T of 5 cm diameter and made tight by rubber gaskets and held together by six bolts. The flanges were secured to 4 com long brass rings into which the glass tube was entered and held gas tight. In a similar way gas stopcocks could be attached along the explosion tube (see Fig. 1).

It was planned at first to place a dividing septum of tissue paper between the steel and the glass tube and then to fill the two sections separately, the steel one with "Knallgas," the glass tube with the explosive mixture to be investigated. But this arrangement was found to affect the measurements and so was discarded and the following procedure carried out: When the tubes had been evacuated by a rotating oil air pump the entire 5-meter long glass tube was filled with the explosive mixture which in time filled the entire tube. The tube C leading from the pump to the steel tube

was now slipped off the stopcock and the explosive mixture allowed to continue flowing through the glass tube and out this opening. At the same time the steel tube was charged with the "Knallgas" which could also flow from this opening. After a short time all stopcocks were closed. At this instant the steel tube was charged with "Knallgas," the glass tube with the explosive mixture. An ignition spark was now passed and a detonation wave propagated from the "Knallgas" mixture into the gaseous mixture in the glass tube. A number of test measurements made of the velocity of the detonation impulse produced by the explosion of the "Knallgas" in the steel tube, when the glass tube was filled with air, confirmed by their constancy the fact that by this method there was secured a known, constant ignition process indispensable to an accurate determination of limiting conditions for the detonation wave in the explosive mixture studied.

3. Time Measurements. Interruption Points.- A ballistic galvanometer connected as shown by the diagram (Fig. 1), with the interruption points spaced from 2.2 to 2.5 meters apart, served to determine the detonation velocity. A detonation wave propagated along the tube will first destroy a delicate conductor in its path and thereby close the battery circuit. In its course it meets and destroys a second conducting filament placed at a known distance from the first and by so doing breaks

the circuit through the galvanometer. During the interval required for the wave to cover the distance between these two points of interruption, the current impulse in the galvanometer has produced a deflection proportional to the quantity of electricity that has passed during this interval. By this means the velocity of propagation of the wave in the gaseous mixture is determined. The current used was taken from an accumulator of 2 to 10 volts.

The device employed by Dixon (Reference 6) as interruption points, also the device made use of by Berthelot and Vieille (Reference 4) was found to be expensive as well as inconvenient. A few trials led me to the following simple and reliable arrangement: A piece of the glass tubing 30 or 40 cm long was provided with two opposite projections fused to its inside surface. These projections were about 1.5 cm long and 1.1 cm wide. A narrow strip of aluminum foil could then be laid horizontally across these projections to bridge the current gap. On the outside of the tube, porcelain cups filled with Wood's metal served as connecting elements. This entire piece of tubing remained permanently attached to the rest of the apparatus. In this way the sensitive piece of foil serving as interruption point could easily and quickly be adjusted in the tube. The first of these interruption bridges was placed 85 cm from the end of the steel section of the tube so that the interval over which the detonation velocity was to be measured lay beyond the region where

irregularities could occur between the "Knallgas" and the explosive mixture in the glass tube. This bridge served to close the circuit; a second bridge 2.5 meters further on served to break it. The distance between these bridges could be read on a millimeter scale attached to the wooden base of the apparatus. A mica condenser (0.1 to 1.1 MF) served to adjust the galvanometer. Before or after every trial this capacity, charged with the electromotive force used was discharged through the galvanometer, and the throw observed was used in evaluating the throw observed in the detonation experiment. If E is the deflection constant of the instrument for 1F, l, the length of the tube between the two interruption points expressed in meters, W, the total resistance in ohms and A the throw of the galvanometer for the experiment, then the velocity of the detonation wave, v, will be given by $v = \frac{E\ l}{A\ W}$. The total resistance of the system was determined from time to time by a sensitive galvanometer and Wheatstone bridge. The electrical instruments were set up in a room adjoining that used for the explosion experiments. The lead wires between the two sets of apparatus were bound together. The use of a ballistic galvanometer for measurements of this kind has been previously employed only in the form of a condenser chronograph (Reference 10); a detailed description of the use of this device in the measurement of detonation velocity is given by R. Becker (Reference 11). The Pouillet connection shown in Figure 1 is more convenient. Both connec-

tions provide good insulation throughout. All of my electrical instruments and their connections come in contact only with glass and porcelain. The set of the galvanometer was uninfluenced by make and break of the circuit by an experiment. If it showed a displacement, the observed results were discarded. The small displacement of the null point before an experiment required only an insignificant correction - less than 0.2%. The use of a ballistic galvanometer as here described avoided the use of exceedingly long lengths of tubing and gave more consistent results than those so far obtained photographically.

4. Extension of the Detonation Tube.- It is true that, on account of self-induction, the Pouillet connection system is not adapted to the measurement of too short time intervals, that is, to lengths of only a few centimeters covered by the detonation wave. In the course of the experimental study it seemed desirable to increase the length of the detonation tube in order to confirm the results obtained with the shorter tube. To this end a steel tube having the same diameter as the glass tube was bent into a half circle of one-half meter diameter and attached to the end of the original tube. To the other end of the steel tube, and thus leading back parallel to the original tube was attached a second length of glass tubing like the first. This second length of tubing was provided with interruption points also like the first, 6.5 meters to 9 meters from the end

of the ignition tube. In order to read both sets of interruption points at the same time, a second galvanometer with its connections was set up. According to the experience of Dixon and of Berthelot, the bend introduced in the length of the detonation tube should be without influence on the speed of the explosive wave. In the arrangement described the tube lengths over which measurements were taken lay well outside this bend in the tube. Those results that showed the speed of the wave to vary over the measuring lengths of the detonation tube were held to be unsatisfactory in all cases of dilute mixtures.

III. Results

1. The "Knallgas" Detonation Wave.- A few velocity measurements were carried out on the rate of propagation of the impact wave resulting from the $2\ H_2 + O_2 \longrightarrow$ explosive wave reaction, first as imparted to a column of air. Tabel I below gives in the first heading the positions and lengths - measured from the end of the steel ignition tube - of the distances over which the velocity of the wave was measured in air.

TABLE I

Velocity in air of the impact wave from the detonation of $2\ H_2 + O_2 \rightarrow$, 1 atmosphere, 18°C

Length measured	80 to 320 cm	652 to 893 cm
Velocity, m/s	675 680 656	423 432 427
Mean	670	427

These values show the mean velocity of the decreasing impact wave in air over the measuring distances given. The observed rate of decrease in velocity of the wave with increasing distance from its origin agrees well with results obtained by quite different means by Vieille (Reference 12). For similar measurements, linear propagation of the wave, see also Vieille (Reference 13); Le Chatelier (Reference 7); Dixon (Reference 14); Dautriche (Reference 15); Becker (Reference 11) in a long tube 22 mm diameter. Although these values have in themselves no unimportant interest, for the purpose in hand they demonstrate the constancy of the reaction employed for the production of ignition in the gaseous mixture to be examined, by an intense impact wave. At first a septum of tissue paper was used to check the diffusion between the Knallgas charge in the steel tube and the gaseous mixture to be examined. Later this practice was dispensed with since the presence of the paper might interfere with the even progress of the wave in the tube. The filling took place in the two sections of the tube in the manner described in a previous paragraph. The initial impulse as the above table shows, was unusually constant. Any small variation between individual impulse values due to different degrees of diffusion, disappeared when, in place of a column of air, a column of an explosive mixture was met. The velocity of the initial wave remained, over the measuring lengths of the tube, above the explosive wave velocity to be expected characteristic of the

gaseous mixture under examination. In the case of a very high initial wave of compression, it could occur that the explosive wave characteristic of the mixture examined could be of less velocity than the initial wave used for ignition. At any rate, the initial impact wave produced by the detonation of $2\ H_2 + O_2 \longrightarrow$ for ignition of the gaseous mixture was not less than the velocity of the explosive wave in any mixture capable of maintaining normal detonation.* Previously the concept of detonation limits has remained so vague that a general definition was not possible. Should one accept the "limiting mixtures" of Le Chatelier, there would remain also much opposing data. On the basis of actual experimental results the question of detonation limits may be satisfactorily answered. The question of the effect of the use of very high impact waves to produce ignition in the gaseous mixtures, will be treated later on.

2. Limiting Conditions for Detonation in Hydrogen-Air Mixtures.- For the investigation of dry hydrogen-air mixtures it was first determined that the mode of ignition just described was adequate. The following table gives the different positions, measured from the ignition tube, of the lengths over which the velocities of the explosive wave were measured:

*Without changing the set-up of the apparatus it was possible to secure an initial impact wave of greater intensity than that resulting from the $2\ H_2 + O_2$ detonation. The combination $2\ C_2H_2 + 3\ O_2 \longrightarrow$ was used.

TABLE II

Dry hydrogen-air mixtures, 1 atmosphere, 18°C

a) Velocity between the first set of interruption points (80 to 330 cm)		b) Velocity between the second set of interruption points (652 to 886 cm)	
% H_2	Velocity m/s	% H_2	Velocity m/s
10.7	824	10.0	470
14.9	963 978	15.3	905
16.3	995	16.6	950
16.5	995	17.6	1003
17.6	1047	18.0	1050
18.3	1207	18.5	1300
18.8	1468 1482	18.8	1483
18.9	1497		
19.6	1620		

At first only the measuring length (a) was used in the apparatus. In this portion of the tube, when the 10% hydrogen mixture was fired, only a weak flame was noticed over a 3-meter length of the tube. Its velocity compared with that of the velocity of the initial impact wave in air was only slightly greater. So small a velocity increase when the compression of the wave is taken into account offers an anomaly that will be referred to in the theoretical part of this paper. A mixture containing 15° hydrogen gave a brighter flame that did not go out. The velocity increased only slowly from a 15% to 17% hydrogen mixture. From an 18% mixture on the flame was very bright and was marked by an exceedingly sharp rise in velocity. In this region it is the writer's opinion that the transition from normal burning to normal detonation should be found. By normal detonation is to be understood every stable quasi-stationary detonation process with

plane wave front; its criterion is the constant rate of propagation over extended distances. This concept of a detonation wave characteristic of an explosive mixture is much more definite than the idea of detonation drawn from isolated values of earlier results. The question of its constancy over extended distances may only be determined by using long tube lengths. The second measuring length in the apparatus described provides means of determining this property of constant velocity. In a 10% hydrogen mixture the indication of flame disappeared before the second measuring distance was reached. Its velocity nevertheless showed some increase over the velocity the wave would have in air. The entire progress of the reaction for this mixture appears as only a slightly modified propagation of the initial ignition wave. It should be noted, however, that this mixture may be ignited by a spark.* In the case of a 15% hydrogen mixture the entire course of the reaction continued throughout the tube so that the velocities over both measuring lengths of the tube could be compared. With an 18% mixture the velocity over the first measuring length was still greater than over the second; but with an 18.5% mixture the same velocity over both measuring lengths appeared and so continued for all mixtures of a higher per cent. Although closely approaching it, the 1100 m/s velocity did not yet mark normal detonation. This seemed first

*Bunte and Eitner (Reference 3) give for the lower limit of ignition of hydrogen-air mixtures, in a 19 mm diameter tube, 9.5%. With increasing tube diameter the ratio air/hydrogen can only fall. See also Mallard and Le Chatelier (Reference 1, p.323).

to be reached with a velocity of 1280 m/s. The data thus obtained would indicate that normal detonation occurred not at the beginning of the sharp rise in velocity from normal burning but further on in the course of this rapid velocity increase. A stable quasi-stationary detonation wave in a hydrogen-air mixture first makes its appearance between 18% and 19% hydrogen content with a velocity of 1250 m/s.

3. Regularity of Limiting Conditions; Explanation of Other Results Found in the Literature.- Since the velocity of propagation of the impact wave near the detonation limit is so sensitive to the composition of the mixture, it is only natural that an impression of irregularity should arise when the composition of each mixture fired was not exactly known. In the earlier results obtained this careful analysis was not always carried out. In other cases, a mixture ratio showing normal detonation may, by the addition of a few mols of inert gas, to dilute it, suddenly exhibit no detonating qualities. Between these two mixtures it might well be there lies a narrow range of steep velocity differences. Over this sensitive range it would be difficult for an apparatus only 100 meters long and with limited measuring lengths to identify these changes. Naturally such a condition offers difficulties to the method employed in this investigation; but by employing two measuring lengths well removed from each other the relative accuracy of the rate determined will be increased. This method at least provides well-defined conditions.

Later on when considering the theoretical side of the problem the data obtained will be more particularly discussed.

4. Carbon Monoxide-Air Mixtures. Detonation below Normal; Instable Detonation.- The behavior of hydrogen-air mixtures may present only a special case. Carbon monoxide-air mixtures are much less brisant and from a practical standpoint are of less interest. Their explosive characteristics are well marked though quite different from those of hydrogen-air. According to Berthelot (Reference 4), dry carbon monoxide-air mixtures could not be made to detonate in a tube 5 mm diameter. But dry mixtures are less explosive than moist ones. Dixon found the detonation velocity of these gases to be profoundly influenced by their water vapor content. Since Dixon did not investigate diluted carbon monoxide mixtures, it is not known if carbon monoxide-air mixtures will support a wave of normal detonation. In order to secure favorable conditions for the examination of these gases, the mixtures were saturated with water vapor at 18°C.* The shorter length of the apparatus was used in these experiments. Table IIIa gives the results obtained.

*From using so damp a mixture, the glass tube was lined with a layer of moisture that allowed some conduction across the points of interruption; this rendered the galvanometer measurements useless. On evacuating the tube the galvanometer readings returned at once to normal. The neighborhood of the interruption points were then provided with resistance heaters so that these points of the tube could be warmed up. This procedure did away with all galvanometer disturbance in using saturated gaseous mixtures.

TABLE IIIa

Carbon monoxide-air mixtures saturated with water vapor at 18°C
Measuring length, 80 to 320 cm

% CO	% O_2	% H_2O	velocity m/s
11.8	17.9		714
18.2	16.6	2 saturated	845
27.0	14.7	at 18°C	935
37.1	12.7		1016
44.0	11.2		1017
53.7	9.2		973

The 11.8% mixture supported a flame only for 1½ meters. This mixture cannot be ignited by an electric spark in tubes 19 mm diameter. Its lower limit according to Bunte and Eitner (Reference 3) is 16.5%. Even an 18.2% mixture supported a flame but a few meters. It is to be presumed that owing to the flow of gases behind the flame the incandescent gases were carried beyond the point the actual flame went out. The graphic representation of these results (Fig. 3) shows a weak velocity maximum near 40% CO, while the stoichiometric mixture calls for 28.7%. The lowest ignition point, according to the data given by Falk (Reference 16) is for the 40% mixture.

In the further measuring length of the tube, for three mixtures showing here a well marked flame, a less velocity was observed.

TABLE IIIb

Carbon monoxide-air mixtures saturated with water vapor at 18°C
Measuring length, 652 to 893 cm

% CO	% O_2	% H_2O	velocity cm/s
37.1	12.7	2.0	955
44.0	11.2	2.0	958

Carbon monoxide-air mixtures, according to these results, are therefore not capable of supporting a normal detonation wave. In these mixtures it is very easy for the compressional wave employed for ignition, and which decreases in velocity with the distance from its origin, to simulate a detonation. This simulation will be the closer in those mixtures having the lowest ignition point. A further consideration of this point, referring also to other gaseous mixtures will be taken up in the theoretical discussion of this problem.

5. Detonation Limits in Mixtures of Carbon Monoxide-Oxygen.- Much better results, together with a notable completion of existing data rewarded the investigation of carbon monoxide-oxygen mixtures. The results are quite different from those obtained with hydrogen-air and the more powerful waves showed unquestionably normal detonation. The gases used were saturated with water vapor. The results of the measurements are given in the following table.

TABLE IV

Carbon monoxide-oxygen mixtures with 2% H_2O at 1 atmosphere and 18°C

a) Length measured, 85 to 325 cm		b)Length measured, 605 to 840 cm	
% CO	velocity m/s	% CO	velocity m/s
12.2	685	23.2	473
22.1	850	35.8	970
29.4	1000	37.7	1035
32.1	1030-1020	38.8	1250
34.7	1026	39.0	1281
37.7	1080		
38.1	1145		
39.2	1347-1335		
50.7	1610		
65.6	1740		

Even the 23% carbon monoxide mixture went out before covering six meters of the tube. The first velocity measurements obtained with this combination were slower than those found for the carbon monoxide-air mixtures. On the other hand, the velocity curve (Fig. 4) shows a bending in the opposite direction and at 37% CO begins to rise sharply but only half as abruptly as in the hydrogen-oxygen mixture at 18% H (Fig. 2). As in that case also, normal detonation was reached in the course of this steep acceleration. With a velocity of 1250 meters per second a normal detonation is indicated while with a velocity of 1100 m/s, a velocity constant has not yet been attained. At water vapor saturation normal detonation in carbon monoxide-oxygen mixtures intervenes between 38% and 39% CO and its velocity is about 1180 m/s. The relation between the observed position and the position indicated by the theory must also be deferred to in Part II of this paper (N.A.C.A. Technical Memorandum No. 554), which follows.

6. Connection with Dixon's Results. Influence of Tube Diameter.- Two measurements were taken at higher CO% composition in order to show the course of the curve above the steep rise of velocities in the neighborhood of 40% CO. These results give opportunity for comparison with Dixon's. A comparison here between results obtained with hydrogen-air mixtures is not made owing to differences in apparatus used; but the following table will show the agreement between his results and mine. The error in my results I assume to be not greater than 2%.

TABLE V

Mixture	Observed velocity m/s, 21 mm tube	Observed results Dixon's mean 13 mm tube
$2\ H_2 + O_2 + 5\ O_2$	1710	1707
$2\ H_2 + O_2 + 5\ N_2$	1840	1815

If the values given by Dixon (Reference 6) for the carbon monoxide-oxygen mixtures be interpolated, my value for the last mixture given would be 1692 m/s. Le Chatelier (Reference 7) calls in question the accuracy of Dixon's result. He found for this mixture, 1900 m/s, and assumed it to be a limit mixture. This result was obtained in a tube of 9 mm diameter. It is plain from Table V that tube diameters above 13 mm have small influence on the impact waves near the limits of detonation. The composition of the limiting mixtures and the velocity at the limit would not be much changed by a change in the tube's diameter so long as it could be assumed that a plane wave front

existed.

The investigation here described was carried out at the Institute for Physical Chemistry of the University of Berlin. For his interest and inspiration I wish to thank my revered instructor, Professor W. Nernst, and also Dr. P. Gunther.

S u m m a r y

An investigation of the conditions pertaining to the limits of detonation in gaseous mixtures have for the first time been carried out. The detonation tube is distinguished above those usually employed by a wider (21 mm) diameter and by the use of a constant, defined and quantitative ignition impulse. A ballistic galvanometer with Pouillet connections replaces advantageously the methods that have previously been employed to measure detonation velocities.

For hydrogen-air, carbon monoxide-air, and carbon monoxide-oxygen the limits of detonation and their accompanying conditions have been quantitatively determined. The results obtained show marked regularity and consistency. Previous results to be found in the literature have been discussed.

The possibility to maintain a detonation wave of constant velocity, imparted to the gaseous mixture by an ignition impact wave, ceases for a definite mixture. Above this mixture two different mixtures give characteristic velocities of quite different values. Below this limit, however, there still exists

mixtures that are explosive. In these mixtures, if intense impact ignition waves have been employed a reaction wave may be set up, even in mixtures that will not support normal detonation, that closely resembles a detonation wave. This seems best shown in the case of carbon-monoxide-air mixtures with lowest ignition point.

The velocity of the detonation wave from $2\ H_2 + O_2 \longrightarrow$ mixtures as propagated in a column of air has been determined. The rate of decrease in velocity observed agrees well with like determinations made by Vieille.

(To be followed by Technical Memorandum No. 554, containing Part II of this article.)

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A, Copper gasometer containing Knallgas ($2H_2+O_2$). B, Washbottles, H_2SO_4 conc. C, Pressure tubing to connect with oil air pump, or with the lead tubing, or with the Gasometer A. D, Spark gap, 3 mm dd. Connections to secondary coil of inductor. E, Steel tube (130 cm long, 21 mm diameter). F, Flanges 5 cm diameter; F_1 to attach tube extension. G, Stopcock at side of tube. H, Wood support, 5 m long. K, Glass extensions 15 mm long, 11 mm inside diameter to hold the aluminum foil. L, Jene hard glass tube, 21 mm diameter, about 3 mm wall thickness. M, Stopcock to manometer. N, Calcium chloride tube. P, Gasometer with gas mixture to be studied. R, Resistance ($R_1=R_2$ about 10^4 ohms). S, Accumulator (2 - 8 volts). T, Ballistic galvanometer (with mirror and telescope).

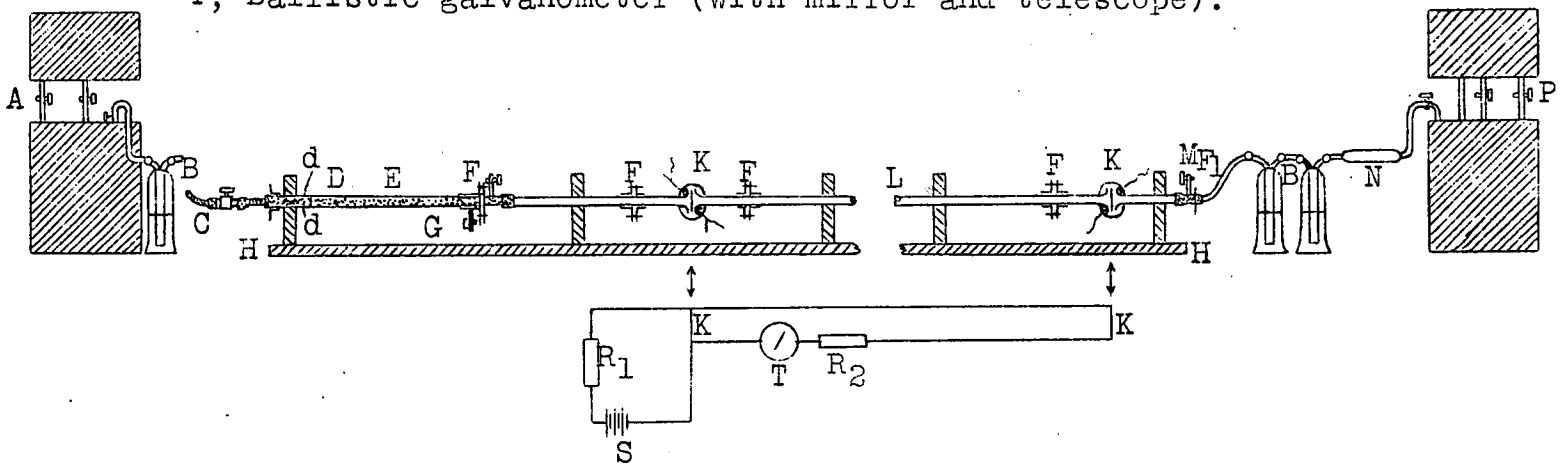

Fig.1 Sketch of the short length of the explosion tube showing connections.